G. P. Christ

The Estimation of the Elements in the R_2O_3 Residue of a Clay Analysis

THE ESTIMATION OF THE ELEMENTS IN THE R_2O_3 RESIDUE OF A CLAY ANALYSIS

BY

GEORGE PHILLIP CHRIST

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

UNIVERSITY OF ILLINOIS

191

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

GEORGE PHILLIP CHRIST

ENTITLED THE ESTIMATION OF THE ELEMENTS IN THE $R_2 O_3$

RESIDUE OF A CLAY ANALYSIS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE in CHEMICAL ENGINEERING

S. A. Braley
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

TABLE OF CONTENTS

THE ESTIMATION OF THE ELEMENTS IN THE $R_2 O_3$ RESIDUE OF A CLAY ANALYSIS

I. INTRODUCTION

The use of cupferron, ammonium nitrosophenylhydroxylamine, as a precipitant for iron was suggested by Oskar Baudisch in 1909, (3). Since then various investigators have used it in quantitative analyses and the results have been excellent in each case. It seems, however, that the value of this reagent in quantitative analysis has not been fully recognized and the present investigation was undertaken to determine its value in ordinary clay analyses. The work consisted of the preparation of known solutions and their analysis by the cupferron method and an analysis of a standard argillaceous limestone sample by the usual method and by the cupferron method.

II. THEORETICAL

Cupferron precipitates iron, titanium, vanadium, zirconium, cerium and copper quantitatively. All these are precipitated from strongly acid solutions except the copper. The fact that copper does not precipitate in acid solution furnishes a method for its separation from iron, (3). The separation of these elements from aluminium, manganese, chromium, nickel, cobalt, zinc, the alkali earths and phosphoric and arsenic acids has been found to be quantitative.

James Brown has shown that cupferron can be used for the analysis of zircon and baddeleyite, (4), and his method was followed in the cupferron analysis. The R2 O3 precipitate of a clay analysis may contain iron, aluminium, titanium, zirconium, chromium, vanadium, phosphorous, the rare earths and manganese if all these are present in the sample. The other elements may be separated from manganese by precipitation in the presence of large amounts of ammonium chloride in case the amount of manganese is small. The cupferron separation depends on the fact that the iron, titanium, zirconium and vanadium are precipitated while the other elements are not. Various methods may then be used for the separation of the elements present in the precipitate and filtrate.

III. PREPARATION OF KNOWN SOLUTIONS

The first experimental work undertaken was the preparation of solutions of iron, aluminium, titanium and manganese, their determination by ordinary methods and then the separation by means of cupferron. The solutions were made up as follows:

Substance	Weight	Volume of solution	Approximate weight of oxide per cc.
$Fe_2\ (SO_4)_3$	2.5745gm	460cc	.002235gm $Fe_2\ O_3$
$Al_2\ (SO_4)_3$	2.0923gm	470cc	.001329gm $Al_2\ O_3$
$K_2\ Ti\ F_6$	1.1133gm	480cc	.000773gm $Ti\ O_2$
$Mn\ SO_4$	1.3672gm	480cc	.001339gm $Mn\ O$

Each of these solutions were then analysed to find the true weight of the element present. The iron, aluminium and titanium were precipitated by means of ammonium hydroxide and ignited to the oxide, (2). The manganese was precipitated and weighed as the pyrophosphate, (2).

Nature of precipitate	Volume of solution	Weight of precipitate		Weight of oxide per cc.
$Fe_2\ O_3$	50cc	.1097gm	.1095gm	.002192gm
$Al_2\ O_3$	50cc	.0650gm	.0653gm	.001303gm
$Ti\ O_2$	50cc	.0385gm	.0386gm	.000771gm
$Mn_2\ P_2\ O_7$	25cc	.0656gm	.0657gm	.001313gm

A solution containing all four of these elements was next made up as follows:

Volume	Solution of	Weight of oxide
200cc	iron	.4384gm
120cc	aluminium	.1564gm
40cc	Titanium	.0308gm
40cc	manganese	.0525gm

IV. ANALYSIS OF KNOWN SOLUTION BY CUPFERRON METHOD

For the analysis, 100cc of the known solution was used. This was equal to a solution of these four elements from one gram of a sample containing 10.96% Fe_2O_3, 3.91% Al_2O_3, .77% TiO_2 and 1.31% MnO.

1. Precipitation of iron and titanium by means of cupferron, (4).

Treat the solution with ammonium hydroxide in slight excess. Add 1:1 sulphuric acid in slight excess and then add 25cc more. Dilute the solution to 150cc and cool with ice. Add 100cc of a 6% aqueous cupferron solution, slowly with constant stirring and filter immediately. Wash 20 times with 1:9 hydrochloric acid. Wash with dilute ammonia until the washings become colorless. Partly dry the precipitate at 80°C., and ignite in a platinum crucible. The ignited precipitate gives the weight of the iron and titanium oxides.

2. Determination of iron and titanium, (1).

The oxides were fused with potassium pyrosulfate and dissolved in sulphuric acid. The iron was determined volumetrically by means of potassium permanganate after reduction with hydrogen sulfide. The titanium was determined by difference.

3. Determination of aluminium and manganese, (4), (2).

Evaporate the filtrate from the cupferron precipitation to about 25cc with 4 50cc portions of concentrated nitric acid. Dilute to 300cc. Precipitate the aluminium by means of ammonium chloride and ammonium hydroxide. Three precipitations were made. The manganese was determined in the filtration by titration against permanganate solution.

V. ANALYSIS OF ARGILLACEOUS LIMESTONE

1. Method of analysis of the U. S. Geological Survey Bulletin #700, (1).

The sample used was sample #1 of the U. S. Bureau of Standards, an argillaceous limestone. The silica was determined in the usual way. The iron, titanium, aluminium and phosphorous were precipitated without manganese in the presence of a large amount of ammonium chloride. The iron was determined volumetrically and the titanium colorimetrically. The combined aluminium and phosphorous were determined by difference.

2. By the cupferron method, (4).

The silica was removed as in the previous analysis. The residue remaining after treatment of the silica with sulphuric and hydrofluoric acids was fused with .5gm of potassium pyrosulphate and the fused mass dissolved in sulphuric acid. This solution was then added to the main solution. The iron, titanium, aluminium and phosphorous were precipitated as hydroxides, (1). After one precipitation the precipitate was dissolved in 100cc 1:7 sulphuric acid. The filtrate was evaporated to a slight precipitate, being kept alkaline with ammonium hydroxide. The precipitate was filtered off and added to the main precipitate. The filtrate was used for the determination of manganese. The iron and titanium were then precipitated from the sulfuric acid solution as in IV,1 & 2. The aluminium was then determined as in IV,3 and the filtrate used for the determination of manganese. The weight of residual silica was determined by the treatment of the aluminium oxide with sulphuric and hydrofluoric acids.

VI. EXPERIMENTAL RESULTS

1. Results of the analysis of known solution by cupferron method.

Analysis for	Weight of oxide taken	Weight of oxide found	
Fe_2O_3	.1096gm	.1094gm	.1095gm
TiO_2	.0077gm	.0079gm	.0080gm
Al_2O_3	.0391gm	.0389gm	.0388gm
MnO	.0131gm	.0127gm	.0125gm

2. Results of the analysis of limestone

Analysis for	Bureau of Standards	Ordinary Method		Cupferron Method	
SiO_2	18.15%	18.13%	18.09%	18.16%	18.18%
Fe_2O_3	1.72%	1.70%	1.76%	1.73%	1.72%
TiO_2	.22%	.24%	.24%	.24%	.23%
Al_2O_3*	5.88%	5.92%	5.97%	5.91%	5.93%
MnO	.04%	.06%	.06%	.04%	.06%

* including P_2O_5

VII. CONCLUSIONS

It appears that the cupferron method is superior to the ordinary method in that it gives a more direct determination of aluminium and obviates the necessity for determining the latter by difference as it is usually determined. The phosphorous is determined in a separate sample and for the true percent of aluminium this must be subtracted from the figures obtained. The cupferron method also obviates the long pyrophosphate fusion involved in the ordinary method and the contamination of the solution with platinum.

VIII. REFERENCES

1. U. S. Geological Survey Bulletin #700
2. Treadwell and Hall, Analytical Chemistry Vol. 2
3. Chem. Zeit. V33 1909 p1298

   Abstract J. C. S. Aii 1910 p76
4. J. Am. C. S. V39 1917 p2358

   Abstract Chem. Abstracts V11 1917 p3190